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RECENT SOVIET WORK IN THE FIELD OF CHEMICAL KINETICS

/The results and methods mentioned in this report are of importance not only in industrial work dealing with the synthesis of chemicals from hydrocarbons, but also from the standpoint of more efficient utilization of fuels and propellants/.

Scientific research in the field of chemical kinetics is one of the traditional activities of the Institute of Chemical Physics, Academy of Sciences USSR. Much has been achieved by the institute in developing new methods for the investigation of complex chemical reactions and in clarifying the nature of intermediate stages which combined together form the total chemical process. A lot of attention was devoted to the study of chain reactions and particularly to that of oxidation chain reactions. In the early years of the activity of the institute, emphasis was placed on relationships which determine the course of such reactions in time. At present the work of investigators connected with the institute deals almost exclusively with the study of the chemical mechanism of complex processes.

After achieving a certain measure of success in solving problems connected with the mechanism of fundamental types of reactions, particularly chain reactions occurring in the gas phase, the institute could tackle the problem of applying the developed concepts, methods, and techniques to the investigation of reactions which are of practical interest.

In doing so, special attention was paid to the investigation of oxidation reactions of hydrocarbons. It is well known that the USSR posesses huge resources as far as natural and industrial hydrocarbons are concerned. Utilization of these resources may in particular proceed along the line of oxidizing hydrocarbon gases into valuable compounds containing oxygen, i.e., aldehydes, alcohols, and carboxylic acids.

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A. B. Nalbandyan, Doctor of Physico-Mathematical Sciences, carried out a series of investigations devoted to the study of the mechanism of photochemical oxidation of the simplest hydrocarbons (methane, ethane, and propane). Using the data obtained in this work, he then turned to the problem of industrial conversion of methane by oxidation.

The development of this practical line of investigation induced a number of new kinetic investigations which are of scientific interest and have had the effect of advancing the whole field of chemical kinetics.

The work of the collaborators of Nalbandyan who were concerned with the study of the photochemical oxidation of hydrocarbons was carried out in close contact with the practical phase of the investigation.

One may mention in this connection that Nalbandyan established the chain character of the photochemical oxidation of methane in the presence of mercury acting as a "sensitizing" agent (catalyst) together with the fact that a high yield of formaldehyde is obtained in this reaction. Eighty percent of the methane is converted into formaldehyde in this reaction, while in the photochemical oxidation of propane at low temperatures there is formation of organic peroxides alone. The results obtained may be very well explained on the basis of the existence of chain mechanisms and participation in them of free radicals.

Interesting results were obtained by N. M. Emanuel', Doctor of Chemical Sciences, and Z. K. Mayzus, who studied the oxidation of propane in the presence hydrogen bromide acting as a homogenous catalyst. Under the circumstances very high yields of acetone (40-50% on the basis of the initial propane) are obtained in the absence of practically any other oxidation products with the exception of propionic acid. In the course of this investigation, new results on catalysis by hydrogen bromide were obtained.

A notable result was obtained in the investigation of the reaction of propene oxidation which was carried out by S. S. Polyak and V. Ya. Shtern, Candidates of Chemical Sciences. These investigators demonstrated that the oxidation of propene proceeds according to a branched chain mechanism with degenerate branches. The intermediate product that is responsible for the degenerate branching is acetaldehyde.

In connection with the general trend towards the study of the mechanism of hydrocarbon oxidation, the question in regard to the elementary reactions entering into the complex process of the oxidation of various hydrocarbons became of particular importance.

L. I. Avramenko, Candidate of Physico-Mathematical Sciences, who has shown in a number of prior investigations that the free hydroxyl group (OH) plays an essential role in oxidation reactions, extended his research to the study of the interaction of a hydroxyl group with various hydrocarbon molecules. In the course of this work, he investigated the interaction of free hydroxyl with acetylene, ethylene, methane, ethane, aldehydes, and other substances. Obviously, the study of hydrocarbon oxidation products which often are formed in very small quantities required the application of new analytical methods and the modification and further extension of old methods. Extensive work in this connection was done by M. B. Neyman, Doctor of Chemical Sciences, who developed and perfected polarographic methods for the determination of many organic substances including peroxides, unsaturated aldehydes and ketones, acetone and other ketones, and organic halogen derivatives. Neyman also obtained interesting data on the mechanism of hydrocarbon oxidation by applying the method of tracer atoms.

The question in regard to the proof of the existence of the radical HO_2 still remains a subject of current work. Thus, V. V. Voyevodskiy, Candidate of Physico-Mathematical Sciences, who investigated in great detail the reaction of the oxidation of hydrogen, demonstrated that results obtained in the study of the upper limit of spontaneous ignition of a hydrogen-oxygen mixture under conditions corresponding to a slow reaction in the vicinity of the thermal limit of ignition and in the latter's induction period, are in quantitative agreement with the concept of the formation of HO_2 radicals in this reaction. Recently, N. M. Emanuel', Doctor of Chemical Sciences, and K. Ye. Kruglyakova got new data on the mechanism of the decomposition of hydrogen perioxide in aqueous solutions. Their results can be explained on the basis of the assumption that this reaction proceeds by a chain mechanism which involves formation of the HO_2 radical.

Voyevodskiy carried out a number of investigations to determine the recombination constants of hydrogen and oxygen atoms on various surfaces. The results of this work have a bearing on questions of heterogenous catalysis and for that reason may be of considerable interest from the point of view of developments in various fields of chemical kinetics. These results, together with those of prior determinations of constants carried out by Avramenko, Nalbandyan, and Candidate of Chemical Sciences N. S. Eniklopov, have already been applied in the analysis of the kinetics of certain chain reactions.

The extremely reliable and exact thermoelectric method for determining the concentration of atomic hydrogen in dilute flames which has been devised by V. N. Kondrat'yev, Corresponding Member of the Academy of Sciences USSR, deserves particular attention. By using this method, the active centers of acetylene and carbon monoxide flames were investigated. It was shown that active centers are formed in considerable concentrations during the reactions in question.

Investigations by Emanuel' and his collaborators dealing with the phenomenon of chilling were completed. In the course of that work, mixtures of aldehydes and oxygen which had been chilled were exploded after renewed heating at temperatures several scores of degrees lower than the usual explosion temperature. The phenomenon of chilling is explained by the formation of intramolecular hydrogen bonds in the hydroperoxides which appear as intermediate products during reaction. In other words, chilling is an example of the kinetic (chemical) manifestation of intramolecular hydrogen bonding. Recently, new results on the formation of the hydrogen bond in propionic acid hydroperoxide were obtained by Aspirant D. G. Knorre. The investigation in question is of interest from the standpoint of the general aim of chemistry to establish the connection between the constitution of substances and their reactive capacity.

Work done by S. S. Medvedyev, Corresponding Member of the Academy of Sciences USSR, and P. S. Shantarovich, Candidate of Chemical Sciences, established that all polymerization processes can be divided into two basic groups as far as their kinetics are concerned: processes for which the reaction mechanism of an unbranched chain is typical and processes which are governed by laws applying to branched chain mechanism.

N. M. Chirkov, Candidate of Chemical Sciences, has made a further contribution to the knowledge of ionic heterogenous processes. In processes of this type the reaction takes place in a thin layer on the surface of the catalyst and proceeds according to the mechanism of ionic catalysis. By using this method, many important reactions can be carried out at high velocities and with high ultimate yields of desired products.

Significant results were obtained by A. A. Koval'skiy, Doctor of Chemical Sciences, and A. M. Markevich, Candidate of Chemical Sciences, in the study of homogeno-heterogenous reactions, i.e., processes in which an important role is played by the wall of the vessel or a solid catalyst while the reaction also proceeds in the volume of the vessel. A number of valuable results obtained by these authors has already been published. Recently, Koval'skiy, by using the method of separate calorimetry of the component homogenous and heterogenous reactions, succeeded in proving that high concentrations of intermediate substances appear in the course of branched chain reactions, for instance, the reaction of ethane oxidation. This conclusion of the chain theory was also confirmed by other methods on other test objects.

This is an incomplete enumeration of results in the field of chemical kinetics that have been obtained recently at the institute of Chemical Physics. The investigations in question have in many respects advanced further than similar work which is being done abroad.

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